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(71) Applicant: **Nippon Mitsubishi Oil Corporation**
Tokyo (JP)

(72) Inventors:
• **Hirano, Hiroyuki, Nippon Mitsubishi Oil Corp.**
Yokohama-shi, Kanagawa-eki 231-0815 (JP)

• **Shimomura, Yuji,**
c/o Nippon Mitsubishi Oil Corp.
Yokohama-shi, Kanagawa-eki 231-0815 (JP)
• **Suda, Satoshi, c/o Nippon Mitsubishi Oil Corp.**
Yokohama-shi, Kanagawa-eki 231-0815 (JP)

(74) Representative: **Avellan-Hultman, Olle et al**
Ehrner & Delmar Patentbyrå AB
Box 10316
100 55 Stockholm (SE)

(54) **Refrigerating machine oil**

(57) The refrigerating machine oils comprise the specific types of oxygen-containing synthetic oil. The re-

frigerating oils have excellent lubricity, miscibility with a refrigerant and stability when used together with a refrigerant containing dimethyl ether.

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Description

[0001] This invention relates to refrigerating machine oils, and more particularly to refrigerating machine oils useful for refrigerating machines using a refrigerant containing dimethyl ether (DME).

Description of the Prior Art

[0002] Due to the recent issues concerning with the ozone shield depletion, the use of conventional refrigerants for refrigerating machine such as CFC (chlorofluorocarbon) and HCFC (hydrochlorofluorocarbon) have been restricted under a regulation. In place of these refrigerants, HFC (hydrofluorocarbon) has been used as such a refrigerant. However, since the HFC refrigerants also has a problem that it is highly potential in earth warming, the search of alternative refrigerants for the fluorocarbon type refrigerants has been progressed. In such a situation, the application of dimethyl ether (DME : $\text{CH}_3\text{-O-CH}_3$) has been drawn considerable attention because of its harmlessness to the environments, safety and availability.

[0003] Properties required for refrigerating machine oils are lubricity, miscibility with refrigerants and safety, but these properties significantly vary, depending on types of coexisting refrigerants. Because DME is different in chemical structure from those of the conventional fluorocarbon type refrigerants, the conventional refrigerating machine oils having been used therewith are not applicable to refrigerating machines using the DME refrigerant, as they are. A refrigerating machine oil having excellent properties required for use with a refrigerant containing DME has not been developed yet.

[0004] In view of the foregoing, an object of the present invention is to provide a refrigerating machine oil which can be used with a DME refrigerant and is superior in lubricity, miscibility with a refrigerant and safety.

[0005] It has now been found after extensive research that use of an oxygen-containing synthetic oil makes it possible to produce a refrigerating machine oil which can be used with a DME refrigerant and is superior in the aforesaid properties.

SUMMARY OF THE INVENTION

[0006] According to the present invention, there is provided a refrigerating machine oil for use with a dimethyl ether (DME) refrigerant, which oil comprises an oxygen-containing synthetic oil.

DETAILED DESCRIPTION OF THE INVENTION

[0007] The refrigerating machine oil according to the present invention comprises an oxygen-containing synthetic oil. Eligible oxygen-containing synthetic oils for the present invention are an ester, an polyoxyalkylene glycol, a polyvinyl ether, a ketone, a polyphenyl ether, silicone, a polysiloxane and a perfluoro ether, among which an ester, a polyoxyalkylene glycol, a polyvinyl ether and a mixture thereof are preferred.

[0008] Eligible esters are an aromatic ester, a dibasic ester, a polyol ester, a complex ester, a polyol carbonate and a mixture thereof.

[0009] The aromatic ester may be an ester of an aromatic carboxylic acid having 1 to 5, preferably 1 to 4, more preferably 1 to 3 valences and an aliphatic alcohol having 1 to 18, preferably 1 to 12 carbon atoms. Specific examples of the aromatic carboxylic acid having 1 to 6 valences are benzoic acid, phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid and a mixture thereof. The aliphatic alcohol having 1 to 18 carbon atoms may be straight-chain or branched. Specific examples of such aliphatic alcohols are methanol, ethanol, straight or branched propanol, straight or branched butanol, straight or branched pentanol, straight or branched hexanol, straight or branched heptanol, straight or branched octanol, straight or branched nonanol, straight or branched decanol, straight or branched undecanol, straight or branched dodecanol, straight or branched tridecanol, straight or branched tetradecanol, straight or branched pentadecanol, straight or branched hexadecanol, straight or branched heptadecanol, straight or branched octadecanol and a mixture thereof.

[0010] Specific examples of the aromatic ester are dibutyl phthalate, di(2-ethylhexyl)phthalate, dinonyl phthalate, didodecyl phthalate, didodecyl phthalate, ditridecyl phthalate, tributyl trimellitate, tri(2-ethylhexyl) trimellitate, trinonyl trimellitate, tridecyl trimellitate, tridodecyl trimellitate and tritridecyl trimellitate.

[0011] Needless to mention, when an aromatic carboxylic acid having at least two valences is used, it may be a simple ester made from one kind of an aliphatic alcohol or a complex ester made from at least two kinds of aliphatic alcohols.

[0012] The dibasic ester may be an ester obtained by reacting a dibasic acid having 5 to 10 carbon atoms such as glutamic acid, adipic acid, pimelic acid, suberic acid, azelaic acid or sebacic acid with a monohydric alcohol having 1 to 15 carbon atoms and a straight or branched alkyl group, such as methanol, ethanol, propanol, butanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol or pentadecanol, or a mixture of

these esters. Specific examples of the ester are ditiidecyl glutarate, di2-ethylhexyl adipate, diisodecyl adipate, ditrid cyl adipate, di2-ethylhexyl sebacate and a mixture thereof.

[0013] The polyol esters may be an ester of a diol or a polyol having 3 to 20 hydroxyl groups and a fatty acid having 6 to 20 carbon atoms. Specific examples of the diol are ethylene glycol, 1,3-propanediol, propylene glycol, 1,4-butanediol, 1,2-butanediol, 2-methyl-1,3-propanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 2-methyl-2-methyl-1,3-propanediol, 1,7-heptanediol, 2-methyl-2-propyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol and 1,12-dodecanediol. Specific examples of the polyol are polyalcohols such as trimethylol ethane, trimethylol propane, trimethylol butane, di-(trimethylol propane), tri-(trimethylol propane), pentaerythritol, di-(pentaerythritol), tri-(pentaerythritol), glycerin, polyglycerin (glycerin dimers to icosomer), 1,3,5-pentaerythritol, sorbitol, sorbitan, sorbitol-glycerin condensate, adonitol, arabitol, xylitol and mannitol, saccharides such as xylose, arabinose, ribose, rhamnose, glucose, fructose, galactose, mannose, sorbose, cellobiose, maltose, isomaltose, trehalose, sucrose, raffinose, gentianose and melezitose, the partially etherified products of these polyalcohols and saccharides; and methylglucoside. Among these, preferred polyol esters are ester of hindered alcohols such as neopentyl glycol, trimethylol ethane, trimethylol propane, trimethylol butane, di-(trimethylol propane), tri-(trimethylol propane), pentaerythritol, di-(pentaerythritol) and tri-(pentaerythritol).

[0014] Although the carbon number of the fatty acid is not particularly restricted, a fatty acid having 1 to 24 carbon atoms is usually used. Among such fatty acids, preferred are those having more than 3 carbon atoms, more preferred are those having more than 4 carbon atoms, further more preferred are those having more than 5 carbon atoms, and the most preferred are those having more than 10 carbon atoms in view of lubricity. In view of miscibility with a refrigerant, preferred fatty acids are those having fewer than 18 carbon atoms, more preferred are those having fewer than 12 carbon atoms, further more preferred are those having fewer than 9 carbon atoms.

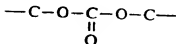
[0015] Furthermore, the fatty acids may be of straight-chain or branched type. In view of lubricity, preferred are straight fatty acids, while in view of hydrolysis stability, preferred are branched fatty acids. The fatty acids may be saturated or unsaturated ones.

[0016] Specific examples of the fatty acid are pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, nonadecanoic acid, icosanoic acid and oleic acid, all of which may be straight or branched or a neo acid where a carbon atom thereof is quaternary. More specific examples of the fatty acid are valeric acid (n-pentanoic acid), caproic acid (n-hexanoic acid), enanthic acid (n-heptanoic acid), caprylic acid (n-octanoic acid), pelargonic acid (n-nonanoic acid), oleic acid (cis-9-octadecenoic acid), isopentanoic acid (3-methylbutanoic acid), 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid.

[0017] The polyol ester may be a partial ester having the hydroxyl groups of the polyol remaining unesterified, a full ester having the hydroxyl groups all of which are esterified or a mixture of the partial ester and the full ester. Preferred are full esters.

[0018] A complex ester used herein denotes an ester obtained by reacting a fatty acid and a dibasic acid with a monohydric alcohol and a polyol. Specific examples of eligible fatty acids, dibasic acids, monohydric alcohols and polyols for the complex ester are the same as those exemplified above with respect to the dibasic esters and the polyol esters.

[0019] A carbonic ester used herein denotes those having the following carbonic ester structure in its molecules;



The carbonic ester may contain one or more of the above structures per molecule.

[0020] Eligible alcohols for the carbonate ester are the above-exemplified aliphatic alcohols or polyols or may be polyglycol and products which can be obtained by the addition reaction of polyglycol with polyol.

[0021] Needless to mention, the esters used herein may be those made from one kind of an ester of single structure or a mixture made from at least two kinds of esters having different structures.

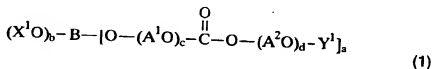
[0022] Among the above exemplified various types of esters, preferred are polyol esters and carbonic esters.

[0023] Among polyol esters, preferred are esters of hindered alcohols such as neopentyl glycol, trimethylolpropane, trimethylolbutane, di-(trimethylolpropane), tri-(trimethylolpropane), pentaerythritol, di-(pentaerythritol) and tri-(pentaerythritol) and more preferred are esters of neopentyl glycol, trimethylolpropane, trimethylolbutane or pentaerythritol, in view of superior hydrolytic stability. Most preferred is an ester of pentaerythritol in view of particular superiority in miscibility with a refrigerant and hydrolytic stability.

[0024] Specific examples of preferred polyol esters are diesters of neopentyl glycol and at least one member selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; triesters of tri-
 5 methylolpropane and at least one member selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; triesters of trimethylolpropane and at least one member selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; triesters of trimethylolbutane and at least
 10 one member selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; and tetraesters of pentaerythritol and at least one member selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid.

[0025] The esters comprising more than two kinds of fatty acids may be a mixture of more than two kinds of esters of one kind of fatty acid and polyol, or an ester of mixed fatty acids of more than two kinds and polyols. The esters of polyol and more than two kinds of fatty acids, particularly mixed fatty acids are superior in characteristics in low temperatures and miscibility with a refrigerant.

[0026] Among the above exemplified carbonic esters, preferred are those having a structure represented by the formula



wherein X^1 is a hydrogen atom, an alkyl group, a cycloalkyl group or a group represented by the formula $Y^2-(OA^3)_n-$ (2) wherein Y^2 is a hydrogen atom, an alkyl group or a cycloalkyl group, A^3 is an alkylene group having 2 to 4 carbon atoms and n is an integer of 1 to 50; A^1 and A^2 may be the same or different from each other and are each independently an alkylene group having 2 to 4 carbon atoms, Y^1 is a hydrogen atom, an alkyl group or a cycloalkyl group, B is a residue of a compound having 3 to 20 hydroxyl groups, a is an integer of 1 to 20 and b is an integer of 0 to 19, with the proviso that $a + b = 3$ to 20, c is an integer of 0 to 50 and d is an integer of 1 to 50.

[0027] In Formula (1), X^1 is a hydrogen atom, an alkyl group, a cycloalkyl group or a group represented by Formula (2). Although not restricted, the alkyl group has generally 1 to 24, preferably 1 to 18, more preferably 1 to 12 carbon atoms. The alkyl group may be straight-chain or branched.

[0028] Specific examples of the alkyl group are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, straight or branched pentyl, straight or branched hexyl, straight or branched heptyl, straight or branched octyl, straight or branched nonyl, straight or branched decyl, straight or branched undecyl, straight or branched dodecyl, straight or branched tridecyl, straight or branched tetradecyl, straight or branched pentadecyl, straight or branched hexadecyl, straight or branched heptadecyl, straight or branched octadecyl, straight or branched nonadecyl, straight or branched icosyl, straight or branched heneicosyl, straight or branched docosyl, straight or branched tricosyl and straight or branched tetracosyl groups.

[0029] Specific examples of the cycloalkyl groups are cyclopentyl, cyclohexyl and cycloheptyl groups.
 [0030] In Formula (2), A^3 is an alkylene group having 2 to 24 carbon atoms. Specific examples of the alkylene group are ethylene, propylene, trimethylene, butylene, tetramethylene, 1-methyltrimethylene, 2-methyltrimethylene, 1,1-dimethylethylene and 1,2-dimethylethylene group.

[0031] In Formula (2), Y^2 is a hydrogen atom, an alkyl group or a cycloalkyl group. Although not restricted, the alkyl group has generally 1 to 24, preferably 1 to 18, more preferably 1 to 12 carbon atoms. The alkyl group may be straight-chain or branched. Specific examples of such alkyl groups are those exemplified with respect to X^1 .

[0032] Specific examples of the cycloalkyl groups are cyclopentyl, cyclohexyl and cycloheptyl groups.

[0033] Y^2 is preferably a hydrogen atom or an alkyl group having 1 to 12 carbon atoms and is more preferably a hydrogen atom or methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, n-hexyl, iso-hexyl, n-heptyl, iso-heptyl, n-octyl, iso-octyl, n-nonyl, iso-nonyl, n-decyl, iso-decyl, n-undecyl, iso-undecyl, n-dodecyl or iso-dodecyl group. a is an integer of 1 to 50.

[0034] X^1 is preferably a hydrogen atom, an alkyl group having 1 to 12 carbon atoms or a group represented by Formula (2). Preferred examples of X^1 are hydrogen atom, methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, n-hexyl, iso-hexyl, n-heptyl, iso-heptyl, n-octyl, iso-octyl, n-nonyl, iso-nonyl, n-decyl, iso-decyl, n-undecyl, iso-undecyl, n-dodecyl or iso-dodecyl group and a group represented by Formula

(2).

[0035] The compounds having 3 to 20 hydroxyl groups and providing a residue for B are the above-exemplified polyols.

[0036] A¹ and A² may be the same or different and are each independently a alkylene group having 2 to 4 carbon atoms. Specific examples of the alkylene group are ethylene, propylene, trimethylene, butylene, tetramethylene, 1-methyltrimethylene, 2-methyltrimethylene, 1,1-dimethylethylene and 1,2-dimethylethylene.

[0037] Y¹ is a hydrogen atom, an alkyl group or a cycloalkyl group. Although not restricted, the alkyl group has generally 1 to 24, preferably 1 to 18, more preferably 1 to 12 carbon atoms. The alkyl group may be of straight or branched chain type. Specific examples of such alkyl groups are those exemplified with respect to X¹.

[0038] Specific examples of the cycloalkyl group are cyclopentyl, cyclohexyl and cycloheptyl groups.

[0039] Y¹ is preferably a hydrogen atom or an alkyl group having 1 to 12 carbon atoms and is more preferably a hydrogen atom or methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, n-hexyl, iso-hexyl, n-heptyl, iso-heptyl, n-octyl, iso-octyl, n-nonyl, iso-nonyl, n-decyl, iso-decyl, n-undecyl, iso-undecyl, n-dodecyl or iso-dodecyl group.

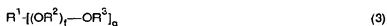
[0040] In Formulae (1) and (2), c, d and e indicate the degree of polymerization at the polyoxyalkylene sites. These polyoxyalkylene sites may be the same or different. In the case where a plurality of different polyoxyalkylene groups are contained, there is no restriction imposed on the polymerization form of oxyalkylene groups and thus it may be random polymerization or block polymerization.

[0041] Although no particular limitation is imposed on the production method of the carbonate esters for use in the present invention, it may be obtained by reacting polyalkylene glycol polyether produced by the addition reaction between a polyol compound and alkyleneoxide, with chloroformate in the presence of an alkali metal hydroxide such as sodium hydroxide and potassium hydroxide, an alkali metal alkoxide such as sodium methoxide and sodium ethoxide or an alkali such as metal sodium at a temperature of 0 to 30 °C. Alternatively, the carbonic ester may be obtained by reacting polyalkylene glycol polyol ester in the presence of the source of carbonic acid such as carbonic acid diester and phosgen, an alkali metal hydroxide such as sodium hydroxide and potassium hydroxide, an alkali metal alkoxide such as sodium methoxide and sodium ethoxide or an alkali such as metal sodium at a temperature of 80 to 150 °C. After this, free hydroxyl groups are etherified as required.

[0042] The product derived from the materials mentioned above may be subjected to refining treatment for removing the by-products and unreacted substances if any. However, small amounts of such by-products and unreacted substances may be present as long as they do not hinder the excellent characteristics of the inventive lubricating oil.

[0043] In the present invention, carbonic ester may be used singly or in the form of a mixture. There is no particular restriction on the molecular weight of the carbonate esters used in the present invention. However, in view of enhancing the sealing performance of a compressor, it is preferred to use those having a number-average molecular weight of preferably 200 to 4,000, more preferably 300 to 3,000. Furthermore, the carbonic ester used in the present invention has a kinematic viscosity at 100 °C of preferably 2 to 150 mm²/s, more preferably 4 to 100 mm²/s.

[0044] Eligible polyoxyalkylene glycols for the refrigerating machine oil of the present invention are a compound represented by the formula



wherein R¹ is a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, an acyl group having 2 to 10 carbon atoms or a residue of a compound having 2 to 8 hydroxyl groups, R² is an alkylene group having 2 to 4 carbon atoms, R³ is a hydrogen atom, an alkyl group having 1 to 10 carbon atoms or an acyl group having 2 to 10 carbon atoms, i is an integer of 1 to 80 and g is an integer of 1 to 8.

[0045] The alkyl group for R¹ and R³ in Formula (3) may be of straight-chain type, branched type or cyclic type. Specific examples of such alkyl groups are methyl, ethyl, n-propyl, straight or branched butyl, straight or branched pentyl, straight or branched hexyl, straight or branched heptyl, straight or branched octyl, straight or branched nonyl, straight or branched decyl, cyclopentyl and cyclohexyl groups. Alkyl groups having more than 10 carbon atoms are not preferred because of their poor miscibility with a refrigerant, leading to phase separation. Therefore, preferred alkyl groups are those having 1 to 6 carbon atoms.

[0046] The alkyl group of the acyl group for R¹ and R³ may be of straight-chain type, branched type or cyclic type. Specific examples of such alkyl groups are the above exemplified alkyl groups having 1 to 9 carbon atoms. Acyl groups having more than 10 carbon atoms are not preferred because of its poor miscibility with a refrigerant, leading to the phase separation thereof. Therefore, preferred acyl groups are those having 2 to 6 carbon atoms.

[0047] In the case where both of R¹ and R³ are an alkyl group or an acyl group, R¹ and R³ may be the same or different from each other. Furthermore, R¹ and R³ may be the same or different in the same molecule when g is 2 or

greater.

[0048] In the case where R^1 is a residue of a compound having 2 to 8 carbon atoms, the compound may be chain or cyclic ones. Specific examples of the compound having 2 hydroxyl groups are ethylene glycol, 1,3-propanediol, propylene glycol, 1,4-butanediol, 1,2-butanediol, 2-methyl-1,3-propanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 2-ethyl-2-methyl-1,3-propanediol, 1,7-heptanediol, 2-methyl-2-propyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol and 1,12-dodecanediol.

[0049] Specific examples of the compound having 3 to 8 hydroxyl groups are polyhydric alcohols such as trimethylololthane, trimethylolpropane, trimethylolbutane, di(trimethylolpropane), tri(trimethylololthane), pentaerythritol, di(pentaerythritol), tri(pentaerythritol), glycerin, polyglycerin (dimer to icosamer consisting of 2 to 20 glycerin monomers), 1,3,5-pentanetriol, sorbitol sorbitan, sorbitol-glycerin condensate, adonitol, arabitol, xylitol and mannitol; saccharides such as xylose, arabinose, ribose, rhamnose, glucose, fructose, galactose, mannose, sorbose, cellobiose, maltose, isomaltose, trehalose, sucrose, raffinose, gentianose and melezitose; the partially etherified products of these polyalcohols and saccharides; and methylglucoside.

[0050] In the present invention, a residue of a compound having hydroxyl groups denotes a residue other than the hydroxyl groups.

[0051] In the present invention, at least one of R^1 or R^2 is preferably an alkyl group, more preferably an alkyl group having 1 to 4 carbon atoms, particularly preferably methyl group in view of viscosity characteristics. Furthermore, for the same reason, both R^1 and R^2 are preferably an alkyl group, more preferably an alkyl group having 1 to 4 carbon atoms, particularly preferably methyl group.

[0052] R^2 in Formula (3) is an alkylene group having 2 to 4 carbon atoms, such as ethylene, propylene and butylene groups. The oxyalkylene group which is a repeating unit represented by (ORF) may be oxyethylene, oxypropylene and oxybutylene groups. The same oxyalkylene groups or more than two different kinds oxyalkylene groups may be present in the same molecule.

[0053] In view of miscibility with a refrigerant and hygroscopicity, the polyoxyalkylene glycol is preferably a copolymer containing an oxyethylene group (EO) and an oxypropylene group (PO). In such a case, the value of EO / (PO + EO) is within the range of preferably 0.1 to 0.6, more preferably 0.3 to 0.6 in view of seizure load and viscosity characteristics.

[0054] In view of hygroscopicity and thermal stability, the value of EO / (PO + EO) is within the range of preferably 0 to 0.5, more preferably 0 to 0.2, most preferably 0, in other words, a homopolymer of oxypropylene.

[0055] In Formula (3), f is an integer of 1 to 80 and g is an integer of 1 to 8. If R^1 is an alkyl group or an acyl group, g is 1. If R^1 is a residue of a compound having 2 to 8 hydroxyl groups, g indicates the number of the hydroxyl groups.

[0056] Although not restricted, the average value of $f \times g$ is preferably to be 6 to 80 so as to fulfill the above described requirements as a refrigerating machine oil.

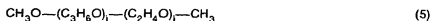
[0057] The polyoxyalkylene glycol of Formula (3) encompasses those having in its terminal ends hydroxyl groups. Such polyoxyalkylene glycols may be used for the inventive lubricating oil if the hydroxyl groups are contained in such an amount that the ratio thereof to all of the end groups is less than 50 mol percent. The hydroxyl group content exceeding 50 mol percent is not preferable because the resulting oil is increased in hygroscopicity and reduced in viscosity index.

[0058] The polyoxyalkylene glycol used for the present invention is preferably a polyoxypropylene glycol dimethyl ether represented by the formula



wherein h is an integer of 6 to 8;

or a polyoxyethylene polyoxypropylene glycol dimethyl ether represented by the formula

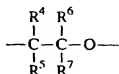


wherein i and j are each an integer of greater than 1 but are such an integer that the total of i and j is within the range of 6 to 80, in view of being economical and effective; and is preferably a polyoxypropyleneglycol monobutyl ether represented by the formula



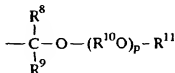
wherein k is an integer of 6 to 80; and a polyoxypropylene glycol diacetate, in view of being economical.

[0059] Furthermore, the polyoxyalkylene glycol may be a polyoxyalkylene glycol derivative having at least one constituting unit represented by the formula



(7)

wherein R⁴ through R⁷ are each independently a hydrogen atom, a monovalent hydrocarbon group having 1 to 10 carbon atoms or a group represented by the formula



(8)

wherein R⁸ and R⁹ are each independently a hydrogen atom, a monovalent hydrocarbon group having 1 to 10 carbon atoms or an alkoxyalkyl group having 2 to 20 carbon atoms, R¹⁰ is an alkylene group having 2 to 5 carbon atoms, an alkyl-substituted alkylene group having 2 to 5 carbon atoms in total or an alkoxyalkyl-substituted alkylene group having 4 to 10 carbon atoms in total, p is an integer of 0 to 20 and R¹¹ is a monovalent hydrocarbon group having 1 to 10 carbon atoms;

and at least one of R⁴ through R⁷ is a group represented by Formula (8).

[0060] In Formula (7), R⁴ through R⁷ are each independently a hydrogen atom, a monovalent hydrocarbon group having 1 to 10 carbon atoms or a group represented by Formula (8). Specific examples of such monovalent hydrocarbon groups are a straight or branched alkyl group having 1 to 10 carbon atoms, a straight or branched alkenyl group having 2 to 10 carbon atoms, a cycloalkyl or alkylcycloalkyl group having 5 to 10 carbon atoms, an aryl or alkylaryl group having 6 to 10 carbon atoms and an arylalkyl group having 7 to 10 carbon atoms. Among these, preferred are monovalent hydrocarbon groups having fewer than 6 carbon atoms and most preferred are those having fewer than 3 carbon atoms, such as methyl, ethyl, n-propyl and isopropyl.

[0061] In formula (8), R⁸ and R⁹ are each independently a hydrogen atom, a monovalent hydrocarbon group having 1 to 10 carbon atoms or an alkoxyalkyl group having 2 to 20 carbon atoms, among which an alkyl group having fewer than 3 carbon atoms and an alkoxyalkylene group having fewer than 6 carbon atoms are preferred. Specific examples of such alkyl groups are methyl, ethyl, n-propyl and isopropyl groups. Specific examples of such alkoxyalkylene groups are methoxymethyl, ethoxymethyl, n-propoxymethyl, isopropoxymethyl, n-butoxymethyl, isobutoxymethyl, sec-butoxymethyl, tert-butoxymethyl, pentoxymethyl (including all isomers), methoxyethyl (including all isomers), ethoxyethyl (including all isomers), propoxyethyl (including all isomers), butoxyethyl (including all isomers), methoxypropyl (including all isomers), ethoxypropyl (including all isomers), propoxypropyl (including all isomers), methoxybutyl (including all isomers), ethoxybutyl (including all isomers) and methoxypropyl groups (including all isomers).

[0062] R¹⁰ is an alkylene group having 2 to 5 carbon atoms, an alkyl-substituted alkylene group having 2 to 5 carbon atoms in total or an alkoxyalkyl-substituted alkylene group having 4 to 10 carbon atoms in total, preferably an alkylene group having 2 to 4 carbon atoms or a substituted ethylene group having fewer than 6 carbon atoms. Specific examples of such an alkylene group are ethylene, propylene and butylenes groups. Specific examples of such a substituted ethylene group are 1-(methoxymethyl)ethylene, 2-(methoxymethyl)ethylene, 1-(methoxyethyl)ethylene, 2-(methoxyethyl)ethylene, 1-(ethoxymethyl)ethylene, 2-(ethoxymethyl)ethylene, 1-methoxymethyl-2-methylethylene, 1,1-bis(methoxymethyl)ethylene, 2,2-bis(methoxymethyl)ethylene, 1,2-bis(methoxymethyl)ethylene, 1-methyl-2-methoxymethyl-ethylene, 1-methoxymethyl-2-methylethylene, 1-ethyl-2-methoxymethylethylene, 1-methoxymethyl-2-ethylethylene, 1-methyl-2-ethoxymethylethylene, 1-ethoxymethyl-2-methylethylene, 1-methyl-2-methoxyethylethylene and 1-methoxyethyl-2-methylethylene groups.

[0063] R¹¹ is a monovalent hydrocarbon group having 1 to 10 carbon atoms. Specific examples of such a hydrocarbon group are a straight or branched alkyl group having 1 to 10 carbon atoms, a straight or branched alkenyl group having 2 to 10 carbon atoms, a cycloalkyl or alkylcycloalkyl group having 5 to 10 carbon atoms, an aryl or alkylaryl group having 6 to 10 carbon groups and an arylalkyl group having 7 to 10 carbon atoms. Among these groups, preferred are

monovalent hydrocarbon groups having fewer than 6 carbon atoms and particularly preferred are alkyl groups having fewer than 3 carbon atoms, such as methyl, ethyl and n-propyl groups.

[0064] In Formula (7), at least one of R^4 through R^7 is a group represented by the Formula (8). However, either one of R^4 or R^6 is a group represented by Formula (8), and the other and R^5 and R^7 are each a hydrogen atom or a monovalent hydrocarbon having 1 to 10 carbon atoms.

[0065] The above-described polyoxyalkylene glycol derivative contains at least one constituting unit represented by Formula (7). More specifically, the polyoxyalkylene glycol derivative may be largely classified into three types: (i) a homopolymer comprising the constituting unit represented by Formula (7), (ii) a copolymer comprising two or more different constituting units represented by Formula (7) and (iii) a copolymer comprising the constituting unit represented by Formula (7) and another constituting unit such as those represented by the formula

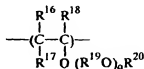


(9)

wherein R^{12} through R^{15} are each independently a hydrogen atom or an alkyl group having 1 to 3 carbon atoms.

[0066] Specific examples of the homopolymer are those having 1 to 200 of constituting units (A) of Formula (7) and the terminal ends each comprising a hydroxyl group, an acyloxy group having 1 to 10 carbon atoms or an alkoxy or allyloxy group having 1 to 10 carbon atoms. Specific examples of the copolymers are those having 1 to 200 of each of the two different constituting units A and B of Formula (7) or having 1 to 200 of constituting units A of Formula (7) and 1 to 200 constituting unit C of Formula (8) and the terminal ends each comprising a hydroxyl group, an acyloxy group having 1 to 10 carbon atoms or an alkoxy or allyloxy group having 1 to 10 carbon atoms. These copolymers may be of any variety, including alternating copolymers, random copolymers and block copolymers each containing the constituting units A and B or C and graft copolymers in which the constituting unit B is graft bonded onto the main chain of the constituting unit A.

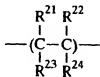
[0067] Eligible polyvinyl ethers for the present invention are polyvinyl ether compounds which contain a constituting unit represented by the formula



(10)

wherein R^{16} , R^{17} and R^{18} are each independently a hydrogen atom or a hydrocarbon group having 1 to 8 carbon atoms and may be the same or different and, R^{19} is a divalent hydrocarbon group having 1 to 10 carbon atoms or a divalent ether bonded oxygen-containing hydrocarbon group having 2 to 20 carbon atoms, R^{20} is a hydrocarbon group having 1 to 20 carbon atoms and q is the value of which average value is 0 to 10; and R^{16} through R^{20} may be the same or different from each other in every constituting unit and in the case where a plurality of $R^{19}O$ are present, they may be the same or different.

[0068] Alternatively, there may be used a polyvinyl ether compounds comprising block or random copolymers having the constituting unit of Formula (10) and a constituting unit represented by the formula



(11)

wherein R^{21} through R^{24} are each independently a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms and may be the same or different, and R^{21} through R^{24} may be the same or different from each other in every constituting unit.

[0069] In formula (10), R^{16} , R^{17} and R^{18} are each independently a hydrogen atom or a hydrocarbon group having 1 to 8, preferably 1 to 4 carbon atoms and may be the same or different. Specific examples of such hydrocarbon groups are an alkyl groups such as methyl, ethyl, n-propyl, isobutyl, sec-butyl, tert-butyl, various types of pentyl, various types of hexyl, various types of heptyl and various types of octyl groups; a cycloalkyl group such as cyclopentyl, cyclohexyl, various types of methylcyclohexyl, various types of ethylcyclohexyl and various types of dimethylcyclohexyl groups; an aryl group such as phenyl, various types of methylphenyl, various types of ethylphenyl and various types of dimethylphenyl groups; and an arylalkyl group such as benzyl, various types of phenylethyl and various types of dimethylbenzyl groups. Particularly preferred for R^{16} , R^{17} and R^{18} is a hydrogen atom.

[0070] In Formula (10), R^{19} is a divalent hydrocarbon group having 1 to 10, preferably 2 to 10 carbon atoms or a divalent ether bonded oxygen-containing hydrocarbon group having 1 to 10 carbon atoms. Specific examples of such a divalent hydrocarbon group having 1 to 10 are a divalent aliphatic group such as methylene, ethylene, phenylethylene, 1,2-propylene, 2-phenyl-1,2-propylene, 1,3-propylene, various types of butylene, various types of pentylene, various types of hexylene, various types of heptylene, various types of octylene, various types of nonylene and various types of decylene groups; an alicyclic group with two bonding sites on the alicyclic hydrocarbon, such as cyclohexane, methylcyclohexane, ethylcyclohexane, dimethylcyclohexane and propylcyclohexane groups; a divalent aromatic hydrocarbon group such as various types of phenylene, various types of methylphenylene, various types of ethylphenylene, various types of dimethylphenylene and various types of naphthylene groups; an alkylaromatic group with a monovalent bonding site on both the alkyl group portion and the aromatic group portion of an alkylaromatic hydrocarbon such as toluene, xylene and ethylbenzene; and an alkylaromatic group with a bonding site on the alkyl group portion of a poly-alkylaromatic hydrocarbon such as xylene and diethylbenzene, of which alkyl group has a bonding. Among these, particularly preferred are aliphatic groups having 2 to 4 carbon atoms.

[0071] Specific examples of the divalent ether bonded oxygen-containing hydrocarbon group having 1 to 10 carbon atoms are methoxymethylene, methoxyethylene, methoxymethylmethylene, 1,1-bis(methoxymethyl)methylene, 1,2-bis(methoxymethyl)methylene, ethoxymethylmethylene, (2-methoxyethoxy)methylmethylene, (1-methyl-2-methoxy)methylmethylene groups. q in Formula (10) represents the number of repeating of $R^{19}O$ and the average value thereof is within the range of 0 to 10, preferably 0 to 5. In the case where a plurality of $R^{19}O$ are present, they may be the same or different from each other.

[0072] R^{20} in Formula (10) is a hydrocarbon group having 1 to 20, preferably 1 to 10 carbon atoms. Specific examples of such a hydrocarbon group are an alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, various types of pentyl, various types of hexyl, various types of heptyl, various types of octyl, various types of nonyl and various types of decyl groups; a cycloalkyl group such as cyclopentyl, cyclohexyl, various types of methylcyclohexyl, various types of ethylcyclohexyl, various types of propylcyclohexyl and various types of dimethylcyclohexyl groups; an aryl group such as phenyl, various types of methylphenyl, various types of ethylphenyl, various types of dimethylphenyl, various types of propylphenyl, various types of trimethylphenyl, various types of butylphenyl and various types of naphthyl groups; and an arylalkyl group such as benzyl, various types of phenylethyl, various types of methylbenzyl, various types of phenylpropyl and various types of phenylbutyl groups. R^{16} through R^{20} may be the same or different from each other in every constituting unit.

[0073] The molar ratio of carbon to oxygen in the polyvinyl ether compound (A) represented by Formula (10) is preferably within the range of 4.2 to 7.0. The molar ratio less than 4.2 results in a compound increased in high hygroscopicity, while the molar ratio exceeding 7.0 results in a compound reduced in miscibility with a refrigerant.

[0074] R^{21} through R^{24} in Formula (11) are each independently a hydrogen or a hydrocarbon group having 1 to 20 carbon atoms and may be the same or different from each other. Specific examples of such a hydrocarbon group are the same as those exemplified above with respect to R^{20} . R^{21} through R^{24} may be the same or different from each other in every constituting unit.

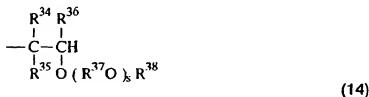
[0075] The polyvinyl ether compound (B) composed of block or random copolymers having the constituting units of Formulae (10) and (11) is preferably within the range of 4.2 to 7.0 in a molar ratio of carbon to oxygen. The molar ratio less than 4.2 results in a compound increased in hygroscopicity, while the molar ratio exceeding 7.0 would result in a compound reduced in miscibility with a refrigerant. In the present invention, it is possible to use a mixture of the above-described polyvinyl ether compounds (A) and (B). These compounds (A) and (B) may be produced by polymerization of the corresponding polyvinyl ether monomer or copolymerization of the corresponding hydrocarbon monomer having an olefinic double bond and the corresponding polyvinyl ether monomer. In the present invention, it is preferred to use the polyvinyl ether compound having the following terminal structure. Namely, it is preferred to use the polyvinyl ether compound having one of the terminal ends represented by the formula



wherein R^{25} , R^{26} and R^{27} are each independently a hydrogen atom or a hydrocarbon group having 1 to 8 carbon atoms and may be the same or different from each other, R^{28} is a divalent hydrocarbon group having 1 to 10 carbon atoms or a divalent hydrocarbon containing ether-bonded oxygen having 2 to 20 carbon atoms, R^{29} is a hydrocarbon group having 1 to 20 carbon atoms and r is the value of which average value is 0 to 10 and in the case where a plurality of R^{28}O is present, they may be the same or different from each other; or represented by the formula



wherein R^{30} , R^{31} , R^{32} and R^{33} are each independently a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms and may be the same or different from each other; and the other end represented by the formula



wherein R^{34} , R^{35} and R^{36} are each independently a hydrogen atom or a hydrocarbon group having 1 to 8 carbon atoms and may be the same or different from each other, R^{37} is a divalent hydrocarbon group having 2 to 20 carbon atoms or a divalent hydrocarbon group containing ether-bonded oxygen and having 2 to 20 carbon atoms, R^{38} is a hydrocarbon group having 1 to 20 carbon atoms, s is the value whose average value is 0 to 10 and in the case where a plurality of R^{37}O is present, they may be the same or different; or by the formula



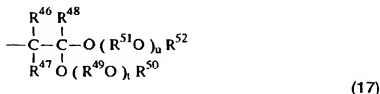
wherein R^{39} , R^{40} , R^{41} and R^{42} are each independently a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms and may be the same or different. Alternatively, it is also preferred to use the polyvinyl ether compound having the terminal ends one of which is represented by Formula (14) or (15) and the other of which is represented by the formula



wherein R^{43} , R^{44} and R^{45} are each independently a hydrogen atom or a hydrocarbon group having 1 to 8 carbon atoms and may be the same or different from each other. Among these polyvinyl ether compounds, the following compounds are particularly suitable for the present invention:

- (i) a compound composed of the constituting unit of Formula (11) wherein R^{16} , R^{17} and R^{18} are hydrogen atoms, the value of q is 0 to 4, R^{19} is a divalent hydrocarbon group having 2 to 4 carbon atoms and R^{20} is a hydrocarbon group having 1 to 20 carbon atoms, and having the terminal ends one of which is represented by Formula (12) or (13) and the other end of which is represented by Formula (14) or (15);
- (ii) a compound composed of the constituting unit of Formula (12) only wherein R^{16} , R^{17} and R^{18} are hydrogen atoms, the value of q is 0 to 4, R^{19} is a divalent hydrocarbon group having 2 to 4 carbon atoms and R^{20} is a hydrocarbon group having 1 to 20 carbon atoms, and having the terminal ends one of which is represented by Formula (13) and the other end of which is represented by Formula (14);
- (iii) a compound composed of the constituting unit of Formula (12) wherein R^{16} , R^{17} and R^{18} are hydrogen atoms, the value of q is 0 to 4, R^{19} is a divalent hydrocarbon group having 2 to 4 carbon atoms and R^{20} is a hydrocarbon group having 1 to 20 carbon atoms, and having the terminal ends one of which is represented by Formula (12) or (13) and the other end of which is represented by Formula (16); and
- (iv) a compound composed of the constituting unit of Formula (12) only wherein R^{16} , R^{17} and R^{18} are hydrogen atoms, the value of q is 0 to 4, R^{19} is a divalent hydrocarbon group having 2 to 4 carbon atoms and R^{20} is a hydrocarbon group having 1 to 20 carbon atoms, and having the terminal ends one of which is represented by Formula (12) and the other end of which is represented by Formula (15).

[0076] In the present invention, it is also capable to use a polyvinyl ether compound composed of the constituting unit of Formula (10) and the terminal ends one of which is represented by Formula (12) and the other end of which is represented by the formula



wherein R^{46} , R^{47} and R^{48} are each independently a hydrogen atom or a hydrocarbon group having 1 to 8 carbon atoms and may be the same or different from each other, R^{49} and R^{51} are each independently a divalent hydrocarbon group having 2 to 10 carbon atoms and may be the same or different from each other, t and u each represents the value of which average value is 0 to 10 and in the case where a plurality of $R^{49}O$ are present, they may be the same or different from each other and in the case where a plurality of $R^{51}O$ are present, they may be the same or different from each other.

[0077] Alternatively, in the present invention, it is also capable to use a polyvinyl ether compound composed of homopolymers or copolymers of an alkylvinyl ether of which average molecular weight is within the range of 300 to 5,000, comprising the constituting unit represented by the formula



wherein R^{53} is a hydrocarbon group having 1 to 8 carbon atoms, or the formula



wherein R^{54} is a hydrocarbon group having 1 to 8 carbon atoms; and having one of the terminal ends represented by

the formula



wherein R^{55} is an alkyl group having 1 to 3 carbon atoms and R^{56} is a hydrocarbon group having 1 to 8 carbon atoms; or the formula



wherein R^{57} is a hydrocarbon group having 1 to 8 carbon atoms.

[0078] The inventive refrigerating machine oil may comprises one or more than two members selected from the above-described oxygen-containing synthetic oil.

[0079] Although not restricted, the content of the oxygen-containing synthetic oil in the inventive refrigerating machine oil is within the range of preferably more than 50 mass percent, more preferably more than 70 mass percent, further more preferably more than 80 mass percent, based on the total mass of the refrigerating machine oil in view of imparting the resulting oil with excellent lubricity, miscibility with a refrigerant, thermal and chemical stability and electric insulation.

[0080] The above-described oxygen-containing synthetic oil may be used in combination with hydrocarbon oils such as mineral oils, olefin polymers, naphthalene compounds and alkylbenzene oils.

[0081] The refrigerating machine oil according to the present invention contains the oxygen-containing synthetic oil and the hydrocarbon oil which is added as required, as a base oil. Although the inventive refrigerating machine oil can be put in use without being blended with any additives, it can be used in the form of a mixture with any of various additives.

[0082] The inventive refrigerating machine oil can be blended with at least one kind of a phosphorus compound selected from the group consisting of phosphoric esters, acidic phosphoric esters, amine salts of acidic phosphoric esters, chlorinated phosphoric esters and phosphorous esters in view of improving the refrigerating apparatus in wear resistance and load resistance by the use of the inventive refrigerating machine oil.

[0083] Specific examples of the phosphoric esters are tributyl phosphate, triphenyl phosphate, trihexyl phosphate, triheptyl phosphate, trioctyl phosphate, trinonyl phosphate, tridecyl phosphate, triundecyl phosphate, tridodecyl phosphate, tritridecyl phosphate, tritetradecyl phosphate, tripentadecyl phosphate, trihexadecyl phosphate, triheptadecyl phosphate, trioctadecyl phosphate, trioleyl phosphate, triphenyl phosphate, tricresyl phosphate, trixylyl phosphate, cresyldiphenyl phosphate and xylyldiphenyl phosphate.

[0084] Specific examples of the acidic phosphoric esters are monobutyl acid phosphate, monopentyl acid phosphate, monohexyl acid phosphate, monoheptyl acid phosphate, monooctyl acid phosphate, monononyl acid phosphate, monodecyl acid phosphate, monoundecyl acid phosphate, monododecyl acid phosphate, monotridecyl acid phosphate, monotetradecyl acid phosphate, monopentadecyl acid phosphate, monohexadecyl acid phosphate, monoheptadecyl acid phosphate, monooctadecyl acid phosphate, monooleyl acid phosphate, dibutyl acid phosphate, dipentyl acid phosphate, diheptyl acid phosphate, dioctyl acid phosphate, dinonyl acid phosphate, didodecyl acid phosphate, didodecyl acid phosphate, ditridecyl acid phosphate, ditetradecyl acid phosphate, dipentadecyl acid phosphate, dihexadecyl acid phosphate, diheptadecyl acid phosphate, dioctadecyl acid phosphate and dioleyl acid phosphate.

[0085] Specific examples of the amine salts of acidic phosphoric esters are methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine, dioctylamine, trimethylamine, triethylamine, tripropylamine, tributylamine, triphenylamine, trihexylamine, triheptylamine and trioctylamine of the acidic phosphoric ester.

[0086] Specific examples of the chlorinated phosphoric esters are tris-dichloropropyl phosphate, tris-chloroethyl phosphate, tris-chlorophenyl phosphate and polyoxyalkylene bis(chloroalkyl) phosphate.

[0087] Specific examples of the phosphorous esters are dibutyl phosphite, dipentyl phosphite, dihexyl phosphite, diheptyl phosphite, dioctyl phosphite, dinonyl phosphite, didodecyl phosphite, didodecyl phosphite, dioleyl phosphite, diphenyl phosphite, dicresyl phosphite, tributyl phosphite, triphenyl phosphite, trihexyl phosphite, triheptyl phosphite, trioctyl phosphite, trinonyl phosphite, tridecyl phosphite, triundecyl phosphite, tridodecyl phosphite, trioleyl phosphite, triphenyl phosphite and tricresyl phosphite.

[0088] Although these phosphorus compounds may be blended with the inventive refrigerating machine oil in any suitable ratio, their contents may be within the range of 0.01 to 5.0 mass percent, preferably 0.02 to 3.0 mass percent,

based on the total mass of the refrigerating machine oil (based on the total mass of the base oil and the whole additives).

[0089] Furthermore, in order to improve the stability of the refrigerating machine oil according to the present invention, it may be blended with at least one kind of an epoxy compound selected from the group consisting of:

(1) phenylglycidyl ether type epoxy compounds, (2) alkylglycidyl ether type compounds, (3) glycidyl ester type epoxy compounds, (4) aryl oxirane compounds, (5) alkyl oxirane compounds, (6) alicyclic epoxy compounds, (7) epoxidized fatty monoesters and (8) epoxidized vegetable oils.

[0090] Specific examples of the phenylglycidyl ether type epoxy compounds (1) are phenylglycidyl ether and alkylphenylglycidyl ethers. The alkylphenylglycidyl ether may be those having 1 to 3 alkyl groups each having 1 to 13 carbon atoms, preferably those having one alkyl group having 4 to 10 carbon atoms. Preferred examples of such alkylphenylglycidyl ethers are n-butylphenylglycidyl ether, i-butylphenylglycidyl ether, sec-butylphenylglycidyl ether, tert-butylphenylglycidyl ether, pentylphenylglycidyl ether, hexylphenylglycidyl ether, heptylphenylglycidyl ether, octylphenylglycidyl ether, nonylphenylglycidyl ether and decylphenylglycidyl ether.

[0091] Specific examples of the alkylglycidyl ether type compounds (2) are decylglycidyl ether, undecylglycidyl ether, dodecylglycidyl ether, tridecylglycidyl ether, tetradecylglycidyl ether, 2-ethylhexylglycidyl ether, neopentylglycidyl ether, trimethylolpropane triglycidyl ether, pentaerythritol tetraglycidyl ether, 1,6-hexanediol diglycidyl ether, sorbitol polyglycidyl ether, polyalkyleneglycol monoglycidyl ether and polyalkyleneglycol diglycidyl ether.

[0092] Specific examples of the glycidyl ester type epoxy compounds (3) are phenylglycidyl ester, alkylglycidyl esters and alkenylglycidyl esters. Preferred are glycidyl-2,2-dimethyloctanoate, glycidyl benzoate, glycidyl acrylate and glycidyl methacrylate.

[0093] Specific examples of the aryl oxirane compounds (4) are 1,2-epoxystyrene and alkyl-1,2-epoxystyrene.

[0094] Specific examples of the alkyl oxirane compounds (5) are 1,2-epoxybutane, 1,2-epoxypentane, 1,2-epoxyhexane, 1,2-epoxyheptane, 1,2-epoxycyclohexane, 1,2-epoxynonane, 1,2-epoxydecane, 1,2-epoxyundecane, 1,2-epoxydodecane, 1,2-epoxytridecane, 1,2-epoxytetradecane, 1,2-epoxypentadecane, 1,2-epoxyhexadecane, 1,2-epoxyheptadecane, 1,2-epoxyoctadecane, 1,2-epoxynonadecane and 1,2-epoxyeicosane.

[0095] Specific examples of the alicyclic epoxy compounds (6) are 1,2-epoxycyclohexane, 1,2-epoxycyclopentane, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, bis(3,4-epoxycyclohexylmethyl) adipate, exo-2,3-epoxynorbornane, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, 2-(7-oxabicyclo[4.1.0] hept-3-yl)-spiro(1,3-dioxane-5,3'-[7]oxabicyclo[4.1.0]) heptane, 4-(1'-metyloxyethyl)-1,2-epoxy-2-methylcyclohexane and 4-epoxyethyl-1,2-epoxycyclohexane.

[0096] Specific examples of the epoxidized fatty monoesters (7) are an ester formed by reacting an epoxidized fatty acid having 12 to 20 carbon atoms with an alcohol having 1 to 8 carbon atoms, phenol or alkylphenol. Particularly preferred are epoxystearates such as butyl, hexyl, benzyl, cyclohexyl, methoxyethyl, phenyl and butylphenyl esters of epoxystearic acid.

[0097] Specific examples of the epoxidized vegetable oils (8) are epoxy compounds of vegetable oils such as soybean oil, linseed oil and cottonseed oil.

[0098] Among these epoxy compounds, preferred are phenylglycidyl ether type epoxy compounds, glycidyl ester type epoxy compounds, alicyclic epoxy compounds and epoxidized fatty monoesters. More preferred are phenylglycidyl ether type epoxy compounds and glycidyl ester type epoxy compounds. Particularly preferred are phenylglycidyl ether, butylphenylglycidyl ether, alkylglycidyl ester and mixtures thereof.

[0099] The inventive refrigerating machine oil may be blended with these epoxy compounds in any suitable blending ratio. The epoxy compound is generally blended in an amount of 0.1 to 5.0 mass percent, preferably 0.2 to 2.0 mass percent, based on the total mass of the refrigerating machine oil (based on the total mass of the base oil and the whole additives).

[0100] Needless to mention, more than two kinds of each of the phosphorus compounds and the epoxy compounds may be used in combination.

[0101] If necessary, in order to further enhance the properties of the refrigerating machine oil of the present invention, it may be blended with suitable conventional additive singly or in combination. The suitable additives may be antioxidants of a phenol type such as di-tert-butyl-p-cresol and bisphenol A or of an amide type such as phenyl- α -naphthyl amine and N,N-di(2-naphthyl)-p-phenylenediamine; anti-wear additives such as zinc dihydrophosphate; extreme pressure agents such as chlorinated paraffin and sulfur compounds; oiliness improvers such as fatty acid; silicone-type antifoaming agents; metal inactivators such as benzotriazole; viscosity index improvers; pour point depressants; and detergent-dispersants. These additives may be added in an amount of less than 10 mass percent, preferably less than 5 mass percent, based on the total mass of the refrigerating machine oil (based on the total mass of the base oil and the whole additives).

[0102] Although there is no particular restriction imposed on the kinematic viscosity of the refrigerating machine oil of the present invention, it preferably has a kinematic viscosity at 40 °C of preferably 3 to 100 mm²/s, more preferably 4 to 50 mm²/s, most preferably 5 to 40 mm²/s and a kinematic viscosity at 100 °C of preferably 1 to 20 mm²/s, more preferably 2 to 10 mm²/s.

[0103] Although not restricted, the refrigerating machine oil of the present invention preferably has a volume resistivity of greater than $1.0 \times 10^{12} \Omega \cdot \text{cm}$, preferably greater than $1.0 \times 10^{13} \Omega \cdot \text{cm}$, more preferably greater than $1.0 \times 10^{14} \Omega \cdot \text{cm}$. When refrigerating machine oils are used in a sealed type refrigerating machine, such volume resistivity is required to be high. The volume resistivity used herein denotes a value measured at a temperature of 40°C in accordance with JIS C 2101 "Testing methods of electrical insulating oils".

[0104] The water content of the refrigerating machine oil of the present invention is not particularly restricted, but may be present within the range of preferably less than 200 ppm, more preferably less than 100 ppm, most preferably less than 50 ppm. When refrigerating machine oils are used in a sealed type refrigerating machine, less water contents are preferred in view of the stability and electric insulation of the oils.

[0105] The total acid value of the refrigerating machine oil of the present invention is not particularly restricted, but may be preferably less than 0.1 mgKOH/g , more preferably 0.05 mgKOH/g in order to prevent the corrosion of metals used in a refrigerating machine or pipes thereof. The total acid value used herein denotes a total acid value measured in accordance with JIS K 2501 "Petroleum products and lubricants-Determination of neutralization number".

[0106] The ash content of the refrigerating machine oil of the present invention is not particularly restricted, but may be preferably less than 100 ppm, more preferably 50 ppm. The ash content used herein denotes a value of ash content measured in accordance with JIS K 2272 "Testing Methods for Ash and Sulfated Ash of Crude Oil and Petroleum Products".

[0107] The refrigerant used in a refrigerating machine together with the refrigerating machine oil is dimethyl ether (DME) or alternatively a mixture of DME and other refrigerants such as hydrofluorocarbon, hydrocarbon, carbon dioxide and ammonia.

[0108] The hydrofluorocarbon refrigerants may be hydrofluorocarbon having 1 to 3 carbon atoms, preferably 1 to 2 carbon atoms. Specific examples of the hydrofluorocarbon refrigerants are difluoromethane (HFC-32), trifluoromethane (HFC-23), pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1-trifluoroethane (HFC-143a), 1,1-difluoroethane (HFC-152a) and a mixture of at least two kinds thereof.

[0109] These refrigerants are suitably selected in accordance with use and performances to be required. Preferred refrigerants are HFC-32 alone; HFC-23 alone; HFC-134a alone; HFC-125 alone; a mixture of HFC-134a / HFC-32 in a ratio of 60-80 mass % / 40-20 mass %; a mixture of HFC-32 / HFC-125 in a ratio of 40-70 mass % / 60-30 mass %; a mixture of HFC-125 / HFC-143a in a ratio of 40-60 mass % / 60-40 mass %; a mixture of HFC-134a / HFC-32 / HFC-125 in a ratio of 60 mass % / 30 mass % / 10 mass %; a mixture of HFC-134a / HFC-32 / HFC-125 in a ratio of 60 mass % / 5-40 mass % and a mixture of HFC-125 / HFC-134a / HFC-32 / HFC-125 in a ratio of 40-70 mass % / 1-15 mass % / 40-60 mass %. More specifically, the HFC refrigerant mixtures include a mixture of HFC-134a / HFC-32 in a ratio of 70 mass % / 30 mass %; a mixture of HFC-32 / HFC-125 in a ratio of 60 mass % / 40 mass %; a mixture of HFC-32 / HFC-125 in a ratio of 50 mass % / 50 mass % (R410A); a mixture of HFC-32 / HFC-125 in a ratio of 45 mass % / 55 mass % (R410B); a mixture of HFC-125 / HFC-143a in a ratio of 50 mass % / 50 mass % (R507C); a mixture of HFC-32 / HFC-125 / HFC-134a in a ratio of 23 mass % / 25 mass % / 52 mass % (R407C); a mixture of HFC-32 / HFC-125 / HFC-143a in a ratio of 25 mass % / 15 mass % / 60 mass % (R407E) and a mixture of HFC-125 / HFC-134a / HFC-143a in a ratio of 44 mass % / 4 mass % / 52 mass % (R404A).

[0110] The hydrocarbon refrigerants may be those which are gaseous at 25°C and one atmospheric pressure. Specific examples of the hydrocarbon refrigerants are alkanes, cycloalkanes and alkenes each having 1 to 5 carbon atoms, preferably 1 to 4 carbon atoms, such as methane, ethylene, ethane, propylene, propane, cyclopropane, butane, isobutane, cyclobutane, methylcyclopropane and a mixture of at least two kinds thereof.

[0111] The blending ratio of DME to hydrofluorocarbon and/or hydrocarbon refrigerants is not particularly restricted. The total amount of hydrofluorocarbon and/or hydrocarbon may be within the range of preferably 1 to 200 parts by weight, more preferably 10 to 100 parts by weight per 100 parts by weight of DME.

[0112] The refrigerating machine oil according to the present invention is generally present in the form of a fluid composition admixed with DME alone or with other refrigerants in a refrigerating machine. The mixing ratio of the inventive refrigerating machine oil to the refrigerants are not particularly restricted, but the refrigerating machine oil may be present in a ratio of 1 to 500 parts by weight, more preferably 2 to 400 parts by weight per 100 parts by weight of the refrigerant.

[0113] The refrigerating machine oil according to the present invention can be used as a lubricating oil for the refrigerant compressors of any types of refrigerating machine. Refrigerating machines to which the inventive refrigerating machine oil is applicable are room air conditioners, packaged air conditioning systems, refrigerators, automobile air conditioners, dehumidifiers, freezers, refrigerating chambers, vending machines, show-cases and cooling systems for chemical plants. Furthermore, the inventive refrigerating machine oil is preferably used in refrigerating machines having sealed compressors. The inventive refrigerating machine oil is also eligible for use in a reciprocating, rotary, or centrifugal type compressor.

[0114] This invention will be further described by way of the following examples which are provided for illustration

purposes only

Examples 1 - 15

- [0115] Sample oils of Examples 1 - 15 were prepared by blending polyol esters and additives shown in Table 1 in accordance with the formulations shown in Tables 2 - 4. Tables 2 - 4 shows the properties (Kinematic viscosity at 40 °C and 100 °C and total acid value) of each of the sample oils.

Table 1

	Alcohol Portion	Fatty Acid Portion
Ester A	Neopentyl glycol	Oleic Acid (100)
Ester B	Neopentyl glycol	2-ethyl hexanoic acid (100)
Ester C	Trimethylol propane	Oleic acid (100)
Ester D	Trimethylol propane	n-octanoic acid (50) n-decanoic acid (50)
Ester E	Trimethylol propane	5,5,5-trimethyl hexanoic acid (100)
Ester F	Penterythritol	n-pentanoic acid (100)
Ester G	Penterythritol	n-pentanoic acid (50) n-heptanoic acid (30) 3,5,5-trimethyl hexanoic acid (20)
Ester H	Penterythritol	2-ethyl hexanoic acid (50) 3,5,5-trimethyl hexanoic acid (50)
Ester I	Dipenterythritol	Oleic acid (100)
Additive a	Phenylglycidyl ether	
Additive b	Tricresyl phosphoric	

[0116] Each of the sample oils was subjected to the following test.

Miscibility Test

[0117] 27 grams of each of the sample oils were blended with 3 grams of a DME refrigerant and then subjected to a test in accordance with "Testing method of evaluating miscibility with a refrigerant" prescribed in JIS K 2211 "Refrigerating machine oils" to observe if the refrigerant and the sample oil would dissolve in each other or if they would be separated from each other or turned into a white-turbid liquid at a temperature of 0 °C. The results are shown in Tables 2 - 4.

Insulation Test

[0118] In accordance with JIS C 2101 "Testing method of electrical insulating oils", a test was conducted to measure the volume resistivity at 25 °C of each of the sample oils. The results are shown in Tables 2 - 4.

Thermal Stability Test

[0119] 90 grams of each of the sample oils, 10 grams of a DME refrigerant and catalysts (wire-shaped iron, copper and aluminum) were charged into an autoclave and heated at 175 °C. After two weeks, a test was conducted so as to observe the appearance of both of the sample oils and the catalysts and measure the volume resistivity and total acid value of each of the sample oils. The results are shown in Tables 2 - 4.

Evaluation Test for Lubricity

[0120] In accordance with ASTM D 2670 "Falex Wear Test", each of the sample oils was subjected to a friction test in which a test machine was run under a load of 250 lb for two hours after being warmed up at an oil temperature of 100 °C under a load of 150 lb for a period of one minute. Each of the sample oils were evaluated by measuring the level of abrasion of the test journal (pin). The results are shown in Tables 2 - 4.

Evaluation Test for Hydrolytic Stability

[0121] 90 grams of each of the sample oils, 0.1 gram of water and 10 grams of a DME refrigerant were taken into a 300 ml glass test tube and then subjected to thermal deterioration at 175 °C for 168 hours in a stainless steel autoclave in which wires made of copper, iron and aluminum were placed as deterioration accelerating catalysts. After this procedure, the total acid value of each of the sample oils was measured. The results are shown with the total acid value prior to the test, in Tables 2 - 4.

Table 2

		Example 1	Example 2	Example 3	Example 4	Example 5
Base oil		Ester A	Ester B	Ester C	Ester D	Ester E
(mass %)		100	100	100	100	100
Additive		-	-	-	-	-
(mass %)						
Kinematic	40°C(mm²/s)	24.2	7.3	48.9	20.2	52.0
Viscosity	100°C (mm²/s)	5.9	2.1	9.7	4.5	7.1
Total acid value (mgKOH/g)		0.00	0.00	0.00	0.00	0.00
Miscibility		Miscible	Miscible	Miscible	Miscible	Miscible
Volume resistivity (Ω·cm)		2.8 × 10 ¹³	1.9 × 10 ¹⁴	8.9 × 10 ¹³	4.5 × 10 ¹³	6.9 × 10 ¹³
Thermal Stability test	Sample oil appearance	Not Changed	Not changed	Not changed	Not Changed	Not Changed
	Catalyst appearance	Not Changed	Not changed	Not changed	Not Changed	Not Changed
	Volume resistivity (Ω·cm)	1.1 × 10 ¹³	9.2 × 10 ¹³	4.6 × 10 ¹³	1.8 × 10 ¹³	3.3 × 10 ¹³
	Total acid value (mgKOH/g)	0.09	0.10	0.08	0.11	0.09
FALEX test	Abrasion wear of pin (mg)	19	21	18	19	17
Hydrolytic stability test	Total acid value (mgKOH/g)	0.20	0.19	0.20	0.21	0.19

Table 3

		Example 6	Example 7	Example 8	Example 9	Example 10
Base oil		Ester F	Ester G	Ester H	Ester I	Ester B(50) Ester H(50)
(mass %)		100	100	100	100	100
Additive		-	-	-	-	-
(mass %)						
Kinematic	40°C(mm ² /s)	15.8	31.6	68.7	107.1	19.2
Viscosity	100°C(mm ² /s)	3.6	5.8	8.4	14.1	3.9

Table 3 (continued)

		Example 6	Example 7	Example 8	Example 9	Example 10
	Total acid value (mgKOH/g)	0.00	0.00	0.00	0.00	0.00
	Miscibility	Miscible	Miscible	Miscible	Miscible	Miscible
	Volume resistivity (Ω -cm)	2.1×10^{14}	5.7×10^{14}	4.9×10^{14}	2.9×10^{14}	3.7×10^{14}
	Thermal Stability Test	Sample oil appearance	Not Changed	Not changed	Not changed	Not Changed
		Catalyst Appearance	Not Changed	Not changed	Not changed	Not Changed
		Volume resistivity (Ω -cm)	1.1×10^{14}	3.5×10^{14}	1.3×10^{14}	1.0×10^{14}
		Total acid value (mgKOH/g)	0.11	0.10	0.09	0.09
	FALEX test	Abrasion wear of pin (mg)	21	18	19	19
	Hydrolytic stability test	Total acid value (mgKOH/g)	0.21	0.22	0.15	0.22

Table 4

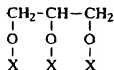
		Example 11	Example 12	Example 13	Example 14	Example 15
	Base oil	Ester G	Ester G	Ester H	Ester H	Ester B(50) Ester H(50)
	(mass %)	99.9	99.9	99.9	99.9	99.9
	Additive	Additive a	Additive b	Additive a	Additive b	Additive a
	(mass %)	0.1	1.0	0.1	1.0	0.1
	Kinematic	40°C (mm ² /s)	31.2	31.0	68.3	67.9
	Viscosity	100°C (mm ² /s)	5.8	5.7	8.4	8.3
	Total acid value (mgKOH/g)	0.00	0.01	0.00	0.01	0.00
	Miscibility	Miscible	Miscible	Miscible	Miscible	Miscible
	Volume resistivity (Ω -cm)	1.9×10^{14}	2.2×10^{14}	3.1×10^{14}	2.0×10^{14}	3.9×10^{14}
	Thermal Stability Test	Sample oil appearance	Not changed	Not changed	Not changed	Not changed
		Catalyst appearance	Not changed	Not changed	Not changed	Not changed
		Volume resistivity (Ω -cm)	3.6×10^{14}	3.5×10^{14}	1.5×10^{14}	1.0×10^{14}
		Total acid value (mgKOH/g)	0.08	0.13	0.06	0.11
	FALEX test	Abrasion wear of pin (mg)	18	8	19	11
	Hydrolytic Stability test	Total acid value (mgKOH/g)	0.03	0.28	0.02	0.17

[0122] As apparent from Tables 2 to 4, the sample oils of Examples 1 to 15 containing a polyether ester as the oxygen-containing synthetic oil specified by the present invention were found to have an excellent lubricity, miscibility with a refrigerant, thermal stability, electric insulation, hydrolytic stability and kinematic viscosity, all of which are well-balanced, when used together with a DME refrigerant.

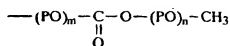
Examples 16 - 22

[0123] The following sample oils were used in Examples 16- 22. Table 5 shows the properties (kinematic viscosity at 100 °C) of each of the sample oils.

Example 16 : Carbonic ester having an average-molecular weight of 1,000 and represented by the formula

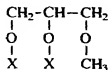


wherein X represents the formula

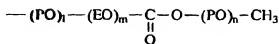


wherein (PO)_m and (PO)_n represent a polyoxypropylene group.

Example 17 : Carbonic ester having an average-molecular weight of 2,000 and represented by the formula

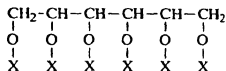


wherein X represents the formula

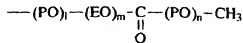


wherein (PO)_h-(EO)_m is a random copolymer of a polyoxypropylene group and a polyoxyethylene group and indicates that the weight ratio therebetween is 90/10 and (PO)_n is a polyoxypropylene group.

Example 18 : Carbonic ester having an average-molecular weight of 2,000 and represented by the formula

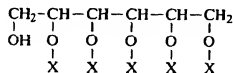


wherein X represents

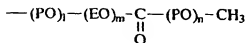


wherein $(PO)_l - (EO)_m$ is a random copolymer of a polyoxypropylene group and a polyoxyethylene group and indicates that the weight ratio therebetween is 90 : 10 and $(PO)_n$ is a polyoxypropylene group.

Example 19 : Carbonic ester having an average-molecular weight of 2,000 and represented by the formula

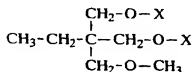


wherein X represents

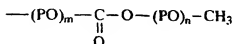


wherein $(PO)_l - (EO)_m$ is a random copolymer of a polyoxypropylene group and a polyoxyethylene group and indicates that the weight ratio therebetween is 90 : 10 and $(PO)_n$ is a polyoxypropylene group.

Example 20 : Carbonic ester having an average-molecular weight of 1,000 and represented by the formula

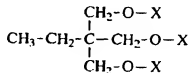


wherein X represents

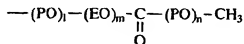


wherein $(PO)_m$ and $(PO)_n$ represent a polyoxypropylene group, respectively.

Example 21 : Carbonic ester having an average-molecular weight of 2,000 and represented by the formula

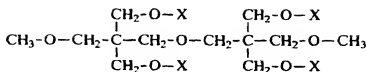


wherein X represents

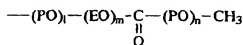


wherein $(PO)_l - (EO)_m$ is a random copolymer of a polyoxypropylene group and a polyoxyethylene group and indicates that the weight ratio therebetween is 90 : 10 and $(PO)_n$ indicates a polyoxypropylene group.

Example 22 : Carbonic ester having an average-molecular weight of 2,000 and represented by the formula



wherein X represents



wherein (PO)_l - (EO)_m is a random copolymer of a polyoxypropylene group and a polyoxyethylene group and indicates that the weight ratio therebetween is 90 : 10 and (PO)_n represents a polyoxypropylene group.

[0124] Each of the above sample oils were subjected to the following test.

Miscibility Test

[0125] 0.5 gram of each of the sample oils were blended with 4.5 grams of a DME refrigerant and then subjected to a test in accordance with "Testing method of evaluating miscibility with a refrigerant" prescribed in JIS K 2211 "Refrigerating machine oils" to observe if the refrigerant and the sample oil would dissolve in each other or if they would be separated from each other or turned into a white-turbid liquid, at a temperature of 0°C. The results are shown in Tables 5.

Insulation Test

[0126] In accordance with JIS C 2101 "Testing method of electrical insulating oils", a test was conducted to measure the volume resistivity at 25 °C of each of the sample oils. The results are shown in Tables 5.

Thermal Stability Test

[0127] 90 grams of each of the sample oils, 10 grams of a DME refrigerant and catalysts (wire-shaped iron, copper and aluminum) were charged into an autoclave and heated at 175 °C. After two weeks, a test was conducted so as to observe the appearance of both of the sample oils and the catalysts and measure the volume resistivity and total acid value of each of the sample oils. The results are shown in Tables 5

Table 5

	Example 16	Example 17	Example 18	Example 19	Example 20	Example 21	Example 22
VIS@100°C	11.5	27.1	32.2	26.4	10.9	28.1	35.2
Volume resistivity	8.3E14	5.4E14	7.1 E14	1.2E13	6.9E14	2.4E14	8.9E13
Miscibility	Miscible	Miscible	Miscible	Miscible	Miscible	Miscible	Miscible
Autoclave test							
Sample oil appearance	Not changed	Not changed	Not changed	Not changed	Not changed	Not changed	Not changed
Catalyst appearance	Not changed	Not changed	Not changed	Not changed	Not changed	Not changed	Not changed
Volume resistivity	4.8E14	5.1E14	2.9E14	3.2E13	3.8E14	7.9E13	1.5E13
Total acid value	0.01	0.02	0.01	0.03	0.01	0.02	0.02

[0128] As apparent from the results in Table 5, the sample oils of Examples 16 to 22 containing a carbonic acid ester as the oxygen-containing synthetic oil specified by the present invention were found to have an excellent lubricity, miscibility with a refrigerant, thermal stability, electric insulation, hydrolytic stability and kinematic viscosity, all of which are well-balanced, when used together with a DME refrigerant.

Examples 23 - 35

[0129] Sample oils of Examples 23 to 35 were prepared by blending polyoxyalkylene glycol (PAG : base oil) or polyvinyl ether (PVE : base oil) shown in Table 6 and additives in accordance with the formulations shown in Tables 7 to 9. Tables 7 to 9 also show the properties (kinematic viscosity at 40 °C and 100 °C and total acid value) of each of the sample oils.

Table 6

		Average Molecular Weight
PAG 1	Polyoxypropylene glycol monomethyl ether	850
PAG 2	Polyoxypropylene glycol dimethyl ether	900
PAG 3	Polyoxyethyleneoxypropylene glycol monomethyl ether (EO / PO = 1 / 9)	950
PAG 4	Polyoxyethyleneoxypropylene glycol monomethyl ether (EO / PO = 3 / 7)	1500
PAG 5	Polyoxyethyleneoxypropylene glycol monobutyl ether (EO / PO = 3 / 7)	1100
PAG 6	Polyoxyethyleneoxypropylene glycol monobutyl ether (EO / PO = 5 / 5)	1200
PAG 7	Polyoxyethyleneoxypropylene glycol dimethyl ether (EO / PO = 3 / 7)	2000
PAG 8	Polyoxyethyleneoxypropylene glycol butylmethyl ether (EO / PO = 1 / 9)	1300
PVE 9	Polyvinylether / Polyvinylisobutyl ether (ethyl / isobutyl = 7 / 1)	900
Additive c	2,6-di-t-butyl-p-cresol	-
Additive d	Phenylglycidyl ether	-
Additive e	Tricresyl phosphate	-

[0130] Each of the sample oils were subjected to the following test.

Miscibility Test

[0131] 0.5 gram of each of the sample oils were blended with 4.5 grams of a DME refrigerant and then subjected to a test in accordance with "Testing method of evaluating miscibility with a refrigerant" prescribed in JIS K 2211 "Refrigerating machine oils" to observe if the refrigerant and the sample oil would dissolve in each other or if they would be separated from each other or turned into a white-turbid liquid, at a temperature of 0 °C. The results are shown in Tables 7 to 9.

Insulation Test

[0132] In accordance with JIS C 2101 "Testing method of electrical insulating oils", a test was conducted to measure the volume resistivity at 25 °C of each of the sample oils. The results are shown in Tables 7 to 9.

Thermal Stability Test

[0133] 90 grams of each of the sample oils, 10 grams of a DME refrigerant and catalysts (wire-shaped iron, copper and aluminum) were charged into an autoclave and heated at 175 °C. After two weeks, a test was conducted so as to observe the appearance of both of the sample oils and the catalysts and measure the volume resistivity and total acid value of each of the sample oils. The results are shown in Tables 7 to 9.

Evaluation Test for Lubricity

[0134] In accordance with ASTM D 2670 "Falex Wear Test", each of the sample oils was subjected to a friction test

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in which a test machine was run under a load of 250 lb for two hours after being warmed up at an oil temperature of 100 °C under a load of 150 lb for a period of one minute. Each of the sample oils was evaluated by measuring the level of abrasion of the test journal (pin). The results are shown in Tables 7 to 9.

Table 7

		Example 23	Example 24	Example 25	Example 26	Example 27
	base oil	PAG 1	PAG 2	PAG 3	PAG 4	PAG 5
	(mass %)	100	100	100	100	100
	additive	-	-	-	-	-
	(mass %)					
	Kinematic 40°C (mm ² /s)	50.5	43.4	45.2	102	48.8
	Viscosity 100°C (mm ² /s)	9.9	9.6	9.3	20.4	10.4
	Total acid value (mgKOH/g)	0.00	0.01	0.01	0.00	0.00
	Miscibility	Miscible	Miscible	Miscible	Miscible	Miscible
	Volume resistivity (Ω-cm)	1.3×10^{11}	7.8×10^{11}	8.9×10^{10}	1.0×10^{11}	1.0×10^{11}
Thermal stability test	Sample oil Appearance	Not changed	Not changed	Not changed	Not changed	Not changed
	Catalyst appearance	Not changed	Not changed	Not changed	Not changed	Not changed
	Volume resistivity (Ω-cm)	4.6×10^{10}	8.5×10^{10}	1.8×10^{10}	1.2×10^{10}	1.0×10^{10}
	Total acid value (mgKOH/g)	0.12	0.09	0.15	0.18	0.20
FALEX test	Abrasion wear of pin (mg)	19	18	17	16	18

Table 8

		Example 28	Example 29	Example 30	Example 31	Example 32
	Base oil	PAG 6	PAG 7	PAG 8	PVE 9	PAG 1
	(mass %)	100	100	100	100	99.5
	Additive	-	-	-	-	Additive c
	(mass %)					0.5
	Kinematic 40°C (mm ² /s)	49.6	135	47.2	65.6	50.4
	Viscosity 100°C (mm ² /s)	10.6	24.8	10.4	8.0	9.9
	Total acid value (mgKOH/g)	0.01	0.01	0.00	0.00	0.00
	Miscibility	Miscible	Miscible	Miscible	Miscible	Miscible
	Volume resistivity (Ω-cm)	4.2×10^{11}	3.3×10^{12}	4.6×10^{12}	3.0×10^{14}	1.3×10^{11}

Table 8 (continued)

5 10	Thermal Stability Test	Sample oil appearance	Not changed	Not changed	Not changed	Not changed	Not changed
		Catalyst appearance	Not changed	Not changed	Not changed	Not changed	Not changed
		Volume resistivity ($\Omega \cdot \text{cm}$)	2.3×10^{10}	1.8×10^{11}	7.2×10^{10}	3.4×10^{13}	7.5×10^{10}
		Total acid value (mgKOH/g)	0.12	0.11	0.09	0.10	0.04
15	FALEX test	Abrasion wear of pin (mg)	17	16	18	17	19

Table 9

		Example 33	Example 34	Example 35		
Base oil		PAG 1	PAG 1	PAG 1		
(mass %)		99.5	99.0	98.0		
Additive		Additive d	Additive e	Additive c	Additive d	Additive e
(mass %)		0.5	1.0	0.5	0.5	1.0
Kinematic	40°C (mm ² /s)	50.4	50.4	50.4		
Viscosity	100°C (mm ² /s)	9.9	9.9	9.9		
Total acid value (mgKOH/g)		0.00	0.00	0.00		
Miscibility		Miscible	Miscible	Miscible		
Volume resistivity ($\Omega \cdot \text{cm}$)		1.3×10^{11}	1.3×10^{11}	1.3×10^{11}		
Thermal Stability Test	Sample oil appearance	Not changed	Not changed	Not changed		
	Catalyst appearance	Not changed	Not changed	Not changed		
	Volume resistivity ($\Omega \cdot \text{cm}$)	7.0×10^{10}	2.0×10^{10}	7.5×10^{10}		
	Total acid value (mgKOH/g)	0.02	0.13	0.03		
FALEX test		Abrasion wear of pin (mg)	19	10	11	

[0135] As apparent from the results in Tables 7 to 9, the sample oils of Examples 23 to 35 containing polyalkylene glycol or polyvinyl ether as the oxygen-containing synthetic oil specified by the present invention were found to have an excellent lubricity, miscibility with a refrigerant, thermal stability, electric insulation, hydrolytic stability and kinematic viscosity, all of which are well-balanced, when used together with a DME refrigerant.

[0136] As described in detail above, the refrigerating machine oil according to the present invention can reach a high level of standard in performances required for a refrigerating machine oil, such as lubricity, miscibility with a refrigerant and thermal stability.

Claims

1. A refrigerating machine oil for use with a refrigerant containing dimethyl ether, which comprises an oxygen-con-

taining synthetic oil.

2. The refrigerating machine oil according to claim 1, wherein said oxygen-containing synthetic oil is selected from the group consisting of an ester, a polyoxyalkylene glycol, a polyvinyl ether, a ketone, a polyphenyl ether, silicone, a polysiloxane and a perfluoro ether.
3. The refrigerating machine oil according to claim 2, wherein said oxygen-containing synthetic oil is selected from the group consisting of an ester, a polyoxyalkylene glycol and a polyvinyl ether.
4. The refrigerating machine oil according to claim 3, wherein said ester is selected from the group consisting of an aromatic ester, a dibasic ester, a polyol ester, a complex ester and a carbonic acid ester.
5. The refrigerating machine oil according to claim 3, wherein said ester is selected from the group consisting of a polyol ester and a carbonic acid ester.
6. The refrigerating machine oil according to claim 3, wherein said polyalkylene glycol is a compound represented by the formula



wherein R^1 is a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, an acyl group having 2 to 10 carbon atoms or a residue of a compound having 2 to 8 hydroxyl groups, R^2 is an alkylene group having 2 to 4 carbon atoms, R^3 is a hydrogen atom, an alkyl group having 1 to 10 carbon atoms or an acyl group having 2 to 10 carbon atoms, f is an integer of 1 to 80 and g is an integer of 1 to 8.

7. The refrigerating machine oil according to claim 3, wherein said polyvinyl ether has constituting units represented by the formula the formula



wherein R^{16} , R^{17} and R^{18} are each independently a hydrogen atom or a hydrocarbon group having 1 to 8 carbon atoms and are the same or different and, R^{19} is a divalent hydrocarbon group having 1 to 10 carbon atoms or a divalent hydrocarbon group containing ether-bonded oxygen and having 2 to 20 carbon atoms, R^{20} is a hydrocarbon group having 1 to 20 carbon atoms and q is the value of which average value is 0 to 10; and R^{16} through R^{20} are the same or different from each other in every constituting unit and in the case where a plurality of $R^{19}O$ are present, they are the same or different.

8. The refrigerating machine oil according to any one of the preceding claims, further comprising a phosphorus compound.
9. The refrigerating machine oil according to any one of the preceding claims, further comprising an epoxy compound.
10. A refrigerating machine fluid composition which comprises the refrigerating machine oil as defined in any one of the preceding claims and dimethyl ether.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 99 85 0142

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Place of search MUNICH		Date of completion of the search 13 January 2000	Examiner Kazemi, P
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